Determination of the Solubility Parameter of Soybean Oil by Inverse Gas Chromatography

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The solubility parameter of soybean oil, δ_2, has been determined by the technique of inverse gas chromatography (IGC). Using soybean oil as the stationary phase, solute retention volumes were precisely determined as a function of temperature using 22 solute probes of varying solubility parameter (δ_1). Solvent (oil)-solute interaction parameters, χ, were also calculated from the solute retention data and indicate complete miscibility of the solute probes with the soybean oil at conditions of infinite dilution. The χ values and their dependence on temperature were used to compute δ_2 at 59, 79, 101, and 123°C. Over this temperature interval, the δ_2 decreased from 7.9 to 6.9 $cal^{1/2}/cm^{3/2}$ with decreasing temperature, a trend consistent with the loss of cohesional energy density in the liquid soybean oil.

Introduction

The regular solution theory, or solubility parameter theory as developed by Hildebrand (1,2), has been used in many areas of technology (3) to explain certain aspects of solution and solubility behavior. The key parameters in this theory are the solubility parameters, which are defined as the square root of the cohesive energy densities of the solute and solvent, respectively (4). A basic tenet of the above theory is that the maximum solubility for a given solute–solvent system is attained when the solubility parameters of the solute and solubility are identical. Therefore a knowledge of the individual solubility parameters for the solute and solvent is required in order to make predictions from this theory.

There are large compendia (5,6) of solubility parameters that are available, in particular for organic solvents that find wide spread use in the chemical industry. Solubility parameters for non-volatile materials, such as polymers, have traditionally been difficult to determine by direct experimental measurement, but have been inferred from solubility measurements of these macromolecules in a variety of solvents having known solubility parameters (7), or from group contribution schemes based on molecular structure correlations (8,9). The development of inverse gas chromatography as a technique for the measurement of polymer solubility parameters (10,11) has also provided an alternative method for the measurement of this data.

In this study, we have used inverse gas chromatography (IGC) to determine the solubility parameter of soybean oil as a function of temperature. IGC has been used by other researchers to determine adsorption isotherms (12), heats of adsorption (13) and the interaction of odoriferous volatile compounds (14) with a variety of

food-related substrates. This study was initiated to determine vegetable oil solubility parameters that are required for the application of solubility parameter theory (SPT) to supercritical fluid extraction (SFE), a technology utilized in our laboratory for the extraction of seed oils. However, the derived data have a far wider application, particularly with respect to predicting and correlating solubility phenomena of naturally-derived oils with and in solvents.

Materials and Methods

Preparation of the chromatographic columns

The chromatographic column used in the IGC measurements was prepared by solvent rinsing a 0.64 cm copper tube, having an approximate length of 1 m. A refined soybean oil sample was obtained from Riceland Foods (Stuttgart, AR) and used as received. The oil was coated on Chromasorb G, 354–250 µm (45/60 mesh), that has been washed with acid and treated with dimethylchlorosilane to eliminate solute adsorption on the 'inert' support. Coating of the column was affected by dissolving the oil in hexane and evaporating the solution carefully with a rotary evaporator.

The coated packings were precisely transferred into the chromatographic columns and conditioned overnight at the highest experimental temperature used in these studies (123°C). The percent oil on the packings was determined by differential gravimetry after calcination of the packing in a muffle furnace. Columns were prepared at three different oil loadings between 5–20 weight percent. Measurement of oil loss during the IGC procedure revealed a negligible weight loss (0.4%).

IGC Instrumentation

A modified Varian Model 1400 gas chromatograph was used for the experimental measurements of solute retention volumes. The major modifications to the gas chromatograph, which was equipped with a flame ionization detector, were the addition of a thermocouple readout device for ascertaining oven/column temperatures and a manometer for accurately determining the column pressure drop. A Hewlett Packard Model 3465B digital multimeter was used for the oven temperature measurements, while a mercury-filled U-tube manometer, connected before the injection port, was used to measure the column pressure drop. Helium was utilized as the carrier gas and its flow rate was measured using a soap bubble flow meter at the head of the column. This flow rate, measured at ambient conditions was then corrected to the average column flow rate according to the procedure of Laub and Pecsok (15). Several flow rate readings were taken throughout the day by diverting the flow from the column, measuring the transit time of the soap bubble under ambient conditions and then computing an average to give the effective daily flow rate, which was subsequently used in the calculations of the retention volumes. Solute peak profiles were recorded on a Omniscribe recorder and the speed of the chart paper checked against periodical stop watch readings.

Choice of solutes

The solutes used in this study were chosen to characterize the stationary phase (soybean oil) and therefore embraced a range of different solubility parameter values. All of the solutes used were reagent grade chemicals. Solute classes chosen for this study included n-alkanes, aromatic hydrocarbons, chlorinated hydrocarbons, aliphatic alcohols and acids. The values of the solubility parameters represented by these solutes ranged from 6.6–13.6 $cal^{1/2}/cm^{3/2}$; adequately bracketing the anticipated solubility parameter of the vegetable oil.

The technique used for injecting the solutes to ensure conditions of infinite dilution of the solute in the stationary phase has been previously described (16). In order to save experimental time, mixtures of the various classes of solutes described above were injected. Column dead volume was determined by measuring the retention volume of a dilute injection of methane into the helium carrier gas.

Results and Discussion

To obtain the solubility parameter of a vegetable oil from IGC measurement requires the computation of intermediate parameters, namely the solute–solvent interaction parameter, χ. The χ parameter is directly derivable from the specific retention volumes measured in the IGC experiment, and although initially derived

for applying IGC to polymeric phases, it can also be used to describe non-polymeric stationary phase (soybean oil) interactions with solutes. Details of the computation of the specific retention volumes are given in standard texts (17) and will not be repeated here. Specific retention volumes, Vg, for the chosen solutes in the soybean oil stationary phase were calculated from the retention time data as described by King et al.(16). These retention volumes were then utilized to compute the interaction parameter, χ, between the solutes and soybean oil according to Equation 1 as (18):

$$\chi = \ln 273.16 \, R/Vg \, M_1 \, p - p^{\circ}_1 \, (B_{11} - \bar{V}_1) \, /RT - \ln \upsilon_1/\upsilon_2 - 1 + \bar{V}_1/M_2 \upsilon_2 \qquad \text{Eqn [1]}$$

where R = 6.236×10^4 mL-mm Hg/mole-°K
M_1 = molecular weight of the solute
p°_1 = vapor pressure of solute at column temperature, T
B_{11} = second pure virial coefficient of the solute at T
v_1 = molar volume of the solute at T
T = column temperature
υ_1 = specific volume of the solute at T
υ_1 = specific volume of the solvent (soybean oil) at T
M_2 = molecular weight of the solvent

It should be noted when IGC is used to determine χ parameters for polymer/solute interaction, that the last two terms in Equation 1 are often eliminated, since they contribute negligibly to χ for the case of an infinitely high molecular weight polymer. This is not the case, however, for a solute having a low molecular weight, such as soybean oil, and these terms have been computed and used in the calculation of χ in this study.

To compute the second virial coefficient of the solute, the well-known relationship developed by McGlashan and Potter (19) as given in Equation 2 was used, where:

$$B_{11}/V_c = 0.430 - 0.866 \, (T_c/T) - 0.694 \, (T_c/T)^2 - 0.0375 \, (n - 1) \, (T_c/T)^{4.5} \qquad \text{Eqn [2]}$$

where T_c = critical temperature of the solute
V_c = critical volume of the solute
n = hypothetical number of carbon atoms for a given solute that yields a p°_1 equivalent to that of a corresponding n-alkane solute.

The parameter n was calculated according to the procedure of Guggenheim and Wormald (20), described previously by King et al. (16). Critical constant data for Equation 2 was obtained from several sources (20–27); however, the critical volume for the solute furfural was obtained from Equation 3 as:

$$V_c = Z_c \, R_c T_c/P_c \qquad \text{Eqn [3]}$$

using a value of 0.26 for the critical compressibility factor, Z_c.

The above procedure was found to give inaccurate virial coefficients for the n-alcohol solutes (16), hence B_{11} values for butanol were taken from the Dymond and Smith compendium (28). Second virial coefficients for methanol, ethanol and isopropanol were calculated using the empirical correlation offered by Kretschmer and Wiebe (29).

Solute vapor pressures in Equation 1 were calculated from the well known Antoine equation (16). Solute molar volumes for Equation 1 were computed from interpolation of plots of solute density as a function of temperature (30) or alternatively by the procedure advocated by Al-Saigh and Munk (31), based on the law of rectilinear diameters.

Solvent (soybean oil) data, M_2 and v_2 required by Equation 1 were obtained as follows. An estimated molecular weight for soybean oil of 870 a.m.u. was computed from lipase hydrolysis data as previously described (16). Molar volume values for soybean oil were calculated from oil densities taken from Bailey's tome (32).

The computed interaction parameters are presented in **Table 1** for 22 solutes at four different temperatures. As noted previously (33), a decreasing value of χ is indicative of enhanced interaction or potential miscibility between the solute and solvent. This trend is exhibited by the following solute classes in **Table 1**: n-alkanes, aromatics, ketones, alcohols, and two of the acids. The chi values for the chlorinated solutes in **Table 1** appear to show a small increase with temperature, indicating a modest demixing with increasing temperature. The observation that χ increases for most of the solutes in **Table 1** is consistent with the well known

fact that solubility increases between solute and solvent over specific ranges of temperature.

The χ values for most of the solutes listed in **Table 1** are below the χ_c, the critical interaction parameter, as defined by Flory (34), and given by Equation 4 as:

$$\chi_c = (1 + x^{1/2})^2/2x \qquad \text{Eqn [4]}$$

where $x = \bar{V}_2/\bar{V}_1$
$\bar{V}_2$ = molar volume of the solvent (soybean oil)

This relationship, which is usually applied to predict miscibility in polymer-solvent systems, can also be extended to the case under study here. The χ_c must be calculated for each solvent (oil)-solute pair from V data and yields χ_cs higher than for the case of infinitely high molecular weight solute (a polymer), for which χ_c is approximately 0.5. Chi values close or below the χ_c value indicate that a condition of miscibility has been achieved for the solute/solvent pair under consideration.

For example, at the experimental temperature 79.0°C, the χ for the n-hexane/soybean oil system is 0.540 and the χ_c value is 6.67. This large difference in χ and χ_c predicts that hexane will be miscible with soybean oil at these very dilute concentrations. Likewise, χ is 2.58 at 79.0°C for the methanol/soybean oil system and the corresponding χ_c is 16.4. Again, the χ_c concept of Flory predicts miscibility between methanol and soybean oil in the limit of infinite dilution for methanol as the solute. This may seem somewhat surprising at first, considering the polarity of methanol relative to the lipophilic soybean oil. However, most of the solute probes used in this study exhibit at least a small finite solubility in the vegetable oil in the limit of infinite dilution. Hence, χ will be smaller than the calculated χ_c for a given solute/oil pair. It should be noted that χ will exhibit a solution compositional dependence, and that the predicted miscibility trends observed at infinite dilution may not be applicable as the mole fraction of solute increases with respect to the soybean oil.

The relative magnitudes of the χ values listed in **Table 1** parallel the order found for the solute activity coefficients at infinite dilution at the same experimental temperatures (16); hence, they can be used as a measure relative solubility of the solute probes in the oil matrix. This is particularly demonstrated by the χ values for the chlorinated hydrocarbons in **Table 1**, which are quite small throughout the temperature range employed in this study. This is a rationale trend since the chlorinated hydrocarbons are excellent solvents for vegetable oils.

There are also some discernible trends in χ with solute molecular structure and solubility parameter in **Table 1**. To a first approximation, χ can be regarded as a sum of a enthalpic and entropic contribution (35), so:

$$\chi = \chi_H + \chi_S = v_1(\delta_1-\delta_2)^2/RT + \chi_S \qquad \text{Eqn [5]}$$

where δ_1 = solubility parameter of the solute
δ_2 = solubility parameter of the solvent (oil)

From Equation 5, it can be seen that the magnitude

Table 1 Interaction parameters for solute/soybean oil systems at specified temperatures

Solute	Temperature (°C)			
	58.6	79.0	100.9	123.4
n-Hexane	0.561	0.540	0.492	0.474
n-Heptane	0.568	0.520	0.473	0.442
n-Octane	1.11	0.954	0.813	0.697
n-Decane	2.36	2.11	1.89	1.70
Cyclohexane	0.411	0.367	0.335	0.318
Benzene	0.232	0.201	0.212	0.165
Toluene	0.162	0.132	0.134	0.118
Ethylbenzene	0.178	0.142	0.140	0.120
Methylene Chloride	0.300	0.288	0.299	0.327
Carbon Tetrachloride	0.150	0.163	0.147	0.157
Trichloroethylene	0.095	0.101	0.105	0.128
Acetone	1.22	1.15	1.06	1.01
Methyl Ethyl Ketone	0.899	0.804	0.771	0.722
Methyl Isobutyl Ketone	0.629	0.582	0.537	0.496
Furfural	1.70	1.49	1.34	1.21
Methanol	2.76	2.58	2.35	2.14
Ethanol	2.41	2.11	1.87	1.66
Isopropanol	1.94	1.68	1.46	1.15
n-Butanol	1.77	1.51	1.28	1.07
Acetic Acid	1.40	1.48	1.50	1.51
Propionic Acid	1.38	1.40	1.36	1.33
Butyric Acid	1.58	1.47	1.40	1.32

of χ_H is dependent on the difference between the solute and solvent solubility parameters. Therefore, the absolute value of δ_H should decrease as the values for the solubility parameters of the solute and solvent become similar. This trend is particularly apparent for the n-alkane solutes, where the value for δ_1 increases from 6.9 to 7.4 $cal^{1/2}/cm^{3/2}$ as the carbon number or hydrophobicity of the solute increases. Likewise, a similar trend is noted for the n-alkanol series, where χ_1 decreases from 13.7 to 11.0 $cal^{1/2}/cm^{3/2}$ in going from methanol to n-butanol; the χ value becomes smaller as the solubility parameter of the solute decreases and the hydrophobicity of the solute increases. These trends suggest that the solubility parameter of soybean oil may lie between 7.4–11.0 $cal^{1/2}/cm^{3/2}$

The χ values computed in **Table 1** can be used to calculate the solubility parameter of the IGC stationary phase (soybean oil) by using Equation 6 (36):

$$(\delta_1^2/RT - \chi/V_1) = (2\delta_1^2/RT)\,\delta_1 - (\delta_2^2/RT + X_S/\bar{V}_1) \quad \text{Eqn [6]}$$

Hence by plotting $(\delta^2_1 RT - \chi/V_1$ (the solubility parameter of the injected solute), one can obtain a value for the slope equal to $2\delta^2_2/RT$ from which the solubility parameter of the stationary phase (soybean oil), δ_2, can be calculated.

Solubility parameters for the solutes used in Equation 6 were taken from Barton (37). The excellent correlation developed by Jayasri and Jaseen (38) was used to compute δ_1 as a function of temperature, where δ_1 at reduced temperature T_2 is computed from δ_1 at a reference reduced temperature of T_1 in Equation 7 as:

$$\delta 1, T_2 = \delta 1, T\,((1 - T_2)/(1 - T_1))^{0.34} \quad \text{Eqn [7]}$$

where $T_1 = T_{ref}/T_c$
$T_2 = T_{exp}/T_c$
T_c = critical temperature of the solute

A plot of Equation 6 is shown in **Fig. 1** for one of the four experimental temperatures (58.66°C) used in this study. A good fit was obtained having a correlation coefficient of 0.9842 (r^2). The somewhat higher scatter of the points representing solutes having higher δ_1 (i.e. acids and alcohols) in **Fig. 1**, may be due to the higher inaccuracy associated with δ_1s for polar, hydrogen bonding solutes. The wide range of solute solubility parameters used in this study along with the excellent correlation coefficients obtained when using Equation 6(r^2 = 0.9842, 0.9837, 0.9813, and 0.9772 for the four temperatures reported in this study) assured that accurate values of χ_2 could be obtained as a function of temperature. As shown in **Table 2**, the error associated with δ_2 is $\pm$ 0.2 $cal^{1/2}/cm^{3/2}$.

The excellent results obtained in this study for the solubility parameter of soybean oil are in contrast to the results obtained by other investigators when using Equation 6 to determine the δ_2 of low molecular solvents. Price (39) had difficulty in obtaining meaningful δ_2s for lower molecular weight compounds, such as plasticizers, when these moieties were employed as the stationary phase in IGC. It was suggested that the

inaccuracies in the δ_2s that were obtained were due to the polar probe solutes deviating from linearity on the plot of Equation 6. However, Price showed that more rational δ_2 values could be obtained by using a modified method that took into account the polar and hydrogen contributions in the calculation of the total δ_2. This approach has recently been used to calculate the δ_2s of surfactants by IGC (40, 41). We believe that part of the problem the above investigators experienced was due to their failure to include the last two terms of Equation 1 in their computation of χ from the experimental retention data, or that gas–liquid surface adsorption effects (42) may also have been prevalent in the retention measurements of the polar probe solutes on the stationary phases they were studying. For this reason, high soybean oil loadings were used in our study, in order to minimize the surface area/volume ratio of the stationary phase in the column proper, which induces adsorption of the polar probe solutes at the gas–liquid interface.

Table 2 lists the solubility parameter for soybean oil as a function of temperature from 59 to 123°C. The values for δ_2 are given in units of $cal^{1/2}/cm^{3/2}$ to allow them to be compared conveniently with older literature values. Conversion of δ_2 to units of MPa from $cal^{1/2}/cm^{3/2}$ (Hildebrand units) can be facilitated by dividing the values in **Table 2** by 2.0455 (43). **Table 2** shows that there is an appreciable drop in the solubility parameter of soybean oil as the experimental temperature increases two-fold. This is not surprising considering the
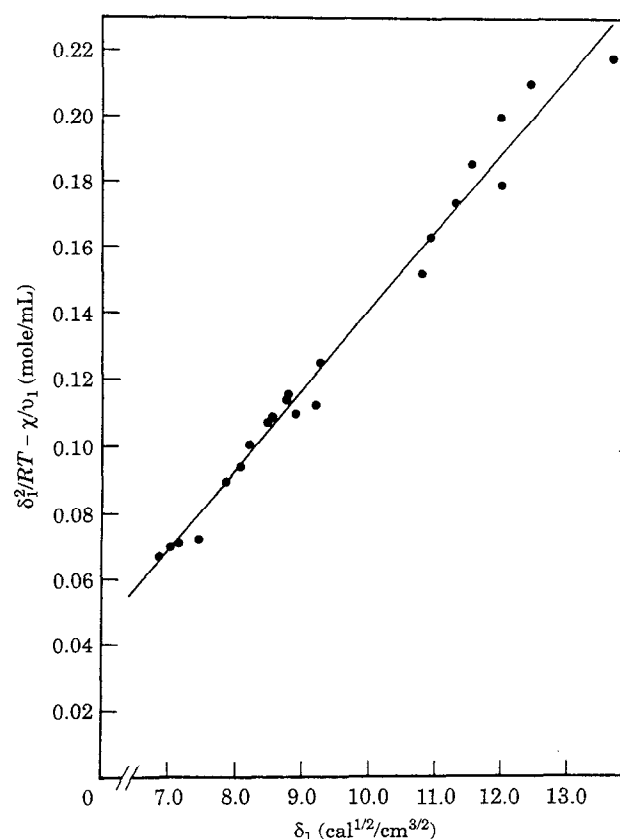

Fig. 1 Determination of the solubility parameter of soybean oil according to Equation [6]

Table 2 Variation in solubility parameters of soybean oil with temperature

Temperature (°C)	Solubility parameter	
	x	Sx
58.7	7.9	0.2
79.0	7.6	0.2
100.9	7.3	0.2
123.4	6.9	0.2

In units of cal $^{1/2}$/cm$^{3/2}$.

loss in cohesional energy density of the oil as temperature is increased. To the author's knowledge, this is the first time that the temperature dependence of the solubility parameter of a vegetable oil has ever been measured.

It is interesting to compare the values of δ_2 given in **Table 2** with the few values available in the literature. Most of literature values are determined or calculated at ambient conditions (20–25°C). The only δs listed in the Barton compendium (44) for vegetable oils are 7.24 (linseed oil) and 9.00 cal$^{1/2}$/cm$^{3/2}$ for castor oil. Computation of the δ_2 for soybean oil using the structural group contribution method of Fedors (9) yielded a value of 8.91 cal$^{1/2}$/cm$^{3/2}$. These values are higher than those listed in **Table 2** due to the higher cohesional energy density of soybean oil at 25°C.

A plot of the solubility parameters for soybean oil v. temperature (**Table 2**) is a monotonic function having a correlation coefficient of –1. This excellent and simple correlation permitted extrapolated values for δ_2 to be determined at 25°C for comparison to literature values. The extrapolated value for δ_2 at 25°C was found to be 8.37 cal$^{1/2}$/cm$^{3/2}$. This is close to the above literature values calculated for soybean oil.

Conclusions

The ability to measure the solubility parameter of a vegetable oil as a function of temperature by IGC is unique, and to the author's knowledge has not been previously reported. Determination of such data will help reduce the paucity of experimental δ_2 in the literature for high molecular weight lipophilic compounds and permit a comparison to values obtained from empirical correlations based on group structural contributions.

From an applied perspective, knowledge of δ_2 can provide some guidance to technologists on the high temperature behavior of neat lipophilic oils and their mixtures with solvents and other oils. For example, the reduction in χ_2 as a function of temperature explains why soybean oil exhibits a higher solubility in supercritical carbon dioxide while undergoing SFE as the temperature of the extraction is increased. Additional IGC on similar lipophilic substrates are currently being conducted and should contribute to the physicochemical database on vegetable oil properties.

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